Lowering of Thermal Reserve Zone Temperature in Blast Furnace by Adjoining Carbonaceous Material and Iron Ore

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The improvement in the efficiency and the decrease in the temperature of reactions in the blast furnace have been required. Among the reactions, the solution loss reaction \((\text{C} + \text{CO}_2 = 2\text{CO})\) is an intensive endothermic reaction and controls the overall reaction inside the blast furnace. To realize the increase in the rate and the decrease in the temperature of the solution loss reaction, a technology to improve the reactivity of carbonaceous material by mixing it into packed ore bed, i.e. a technology to improve the reactivity by adjoining carbonaceous material and iron ore was fundamentally investigated.

Various kinds of carbonaceous materials were mixed into the packed ore bed and the starting temperature for the endothermic reaction equivalent to the solution loss reaction was measured on the basis of the principle of differential thermal analysis. Small size coke and carbon composite iron ore agglomerate as carbonaceous materials were mixed into the ore bed and the effect of carbon content in the ore bed and the effect of the degree of contact between carbonaceous material and iron ore were investigated. The following results were obtained.

1. Introduction

In order to meet the demand for the improved reaction efficiency and low reaction temperature in the blast furnace ironmaking process, recently, fundamental researches on the reactions in the blast furnace are coming into the limelight. In particular, investigations to increase the reaction rate and to lower the reaction temperature in the solution loss reaction are actively being made because the reaction is an intensive endothermic reaction and controls the reactions inside the furnace. As a means to realize the demand, a technology to improve the reactivity of carbonaceous material itself and, in addition, to increase the rate of the solution loss reaction interacting with the reduction reaction by adjoining carbonaceous material and iron ore attracts lots of attention.

As for the interaction between the reduction reaction and the solution loss reaction, a wide variety of researches have been reported such as fundamental researches on the mechanism of reaction \(\text{C} + \text{CO}_2 = 2\text{CO}\) and researches on the actual means to adjoining carbonaceous material and iron ore. As for the latter researches, researches on the process to mix small size coke into ore bed \(^{3,4}\) on the carbon composite iron ore agglomerate \(^{2,5-8}\), a type of raw material made by incorporating carbonaceous material into iron ore agglomerate, and researches for increasing the degree of contact between carbonaceous material and iron ore by utilizing mechanical milling \(^{9,10}\). It has been made clear by these fundamental researches that if the degree of contact between carbonaceous material and iron ore could be increased up to an ideal level, the starting temperature of the solution loss reaction could be lowered.

In the thermal reserve zone temperature, the rate of temperature rise of the materials charged into the blast furnace becomes minimum. The temperature in the thermal reserve zone is approximately equal to the starting temperature of the solution loss reaction, which is an intensive endothermic reaction. If the starting temperature of the reaction, namely the thermal reserve zone temperature, can be lowered, the equilibrium concentration of FeO–Fe reduction reaction will be shifted to higher CO gas utilization efficiency, resulting in the improved CO gas utilization efficiency at the furnace top and the decreased the reducing agents rate. This phenomenon was explained \(^{11}\) by means of...
Fe–C–O equilibrium diagram and Rist diagram.\(^{11)}\) It was also demonstrated experimentally that this phenomenon could be realized by using high reactivity coke\(^{12)}\) or carbon composite iron ore agglomerate.\(^{3)}\) However, these raw materials and fuels are not yet put into practical use because of their difficulty of production. In order to produce them on a commercial basis, some effective means such as utilizing the existing raw materials and fuels, use of small amount of them, or a means to mix them into blast furnace ore bed in small amounts are required.

As an example of practical use of adjoining process of carbonaceous material to iron ore utilizing existing raw materials and fuels, there is a process in which small size coke is mixed into the ore bed. Figure 1 shows the relationships between furnace temperature and gas composition as plotted in the Fe–C–O system equilibrium diagram, which was obtained by a test to use much amount of small size coke in No. 2 Blast Furnace of Kakogawa Works.\(^{3)}\) It can be seen that when small size coke is mixed into the ore bed, with the increase in the amount of small size coke, the thermal reserve zone temperature decreases, resulting in the improved CO gas utilization efficiency. But, although the small size coke rate is increased from 30 kg/THM to 100 kg/THM, the thermal reserve zone temperature is decreased only by about 50°C. For further decrease in the thermal reserve zone temperature, further improvement in the degree of contact between carbonaceous material and iron ore is required. However, the effects of the degree of contact between carbonaceous material and iron ore and the mixing rate of carbonaceous material into ore bed upon the decrease in the thermal reserve zone temperature are not yet known.

In this study, various kinds of carbonaceous materials were mixed into the packed ore bed to adjoin carbonaceous materials and iron ore. On the basis of the principle of differential thermal analysis, the starting temperature for the solution loss reaction was measured. In addition, the effects of carbon content in the ore bed and the degree of contact between carbonaceous material and iron ore upon the starting temperature of the reaction were fundamentally investigated.

2. Experimental Procedure

2.1. Experimental Apparatus

Because the thermal reserve zone temperature in the blast furnace is approximately consistent with the starting temperature of the solution loss reaction of coke, which involves intensive endothermic reaction, the thermal reserve zone temperature of the packed ore bed was measured on the basis of the principle of differential thermal analysis.

Figure 2 shows the experimental apparatus. In the usual differential thermal analysis, a small cell with a diameter and a height of about 5 mm is filled with sample of about several tens of milligram and a measurement is made. In order to make measurement under a condition simulating the packed ore bed, an apparatus with the following dimensions was developed. The reaction tube had an inner diameter of 140 mm and the sample basket had a diameter of 120 mm and a height of 150 mm. The standard material was a φ10 mm alumina ball. The top end of thermocouple was set at the center of the height and the width of the sample bed and standard material bed.

2.2. Sample

Table 1 shows the physical and chemical properties of samples.

The ore bed consists of mixture of sinter (S) and iron ore pellets (IO-P). The size of both of sinter and iron ore pellets was 9.5–13.2 mm, equivalent to that of the standard materi-
The ratio sinter/iron ore pellet was a constant of 54/46 mass%.

As carbonaceous materials to mix into the ore bed, carbon composite iron ore hot briquets (CIO-B) and small size coke (S-C) were used. The carbon composite iron ore hot briquets were produced with the apparatus and process as shown in previous report study. The briquets were produced utilizing thermal plasticity of coal without using binder. As a result, carbon composite iron ore agglomerate with high degree of contact between carbonaceous material and iron ore could be obtained. The briquets contained carbon higher than stoichiometrically required for reduction. The briquets were oval-shaped and had the dimensions of $l=30\, \text{mm}$, $w=25\, \text{mm}$, and $t=17\, \text{mm}$ and were cut into specimens with the size of $9.5–19.1\, \text{mm}$. The size of the small size coke was $9.5–13.2\, \text{mm}$. As compared with the size of sinter and iron ore pellets, the size of the briquets is a little larger and that of the small size coke is equivalent.

Figure 3 schematically shows the state of contact between carbonaceous material and iron ore when the small size coke and the carbon composite iron ore hot briquets as carbonaceous materials are mixed into the ore bed. The degree of contact between carbonaceous material and iron ore becomes lower in the order, (A), (B), (C): (A) The entire ore bed consists of the carbon composite iron ore agglomerate; (B) The carbon composite iron ore agglomerate is mixed into the ore bed; (C) The small size coke is mixed into the ore bed. In the case of (A), carbonaceous material and iron ore powder with the size of about $40\, \mu\text{m}$ are in close contact inside the carbon composite iron ore agglomerate. In the case of (B), in addition to the contact inside the carbon composite iron ore agglomerate, the carbonaceous material in the carbon composite iron ore agglomerate contacts with sinter or iron ore pellets. In the case of (C), although the small size coke is in contact with sinter and iron ore pellets, the mode of contact is point-contact because of its large particle size. Therefore, the degree of contact is low. Among the carbon composite iron ore agglomerates, the hot briquetted agglomerate used in this experiment (Photo (a) in Fig. 3) has the advantage of a higher degree of contact between carbonaceous material and iron ore and a low porosity (about 13%) as compared with the cold briquetted agglomerate (Photo (b)).

Using these samples and mixing methods, the effects of carbon content in the ore bed and the degree of contact between carbonaceous material and iron ore upon the starting temperature of the endothermic reaction were investigated in this study.

2.3. Experimental Conditions

Figure 4 shows the experimental conditions. The rate of temperature rising for the standard material is a constant of $5^\circ\text{C}/\text{min}$. The gas composition is set to the constant pattern, which simulate those of actual blast furnace.

2.4. Experimental Procedure

The standard material was heated from room temperature to $1250^\circ\text{C}$ under the above conditions. The temperatures of the standard material and the sample were measured simultaneously and the difference in both of the temperatures was obtained. The starting temperature of the endothermic reaction of the sample was obtained from extrapolated starting temperature.

3. Experimental Results and Discussion

3.1. Development of Experimental Procedure and Examination of Its Validity

The experiment was made using the specimens in Table 1 and the apparatus shown in Fig. 2. As compared with the conditions in conventional differential thermal analysis, it has the following two features: (a) the sample is solid packed bed; and (b) the sample and the apparatus are large. Therefore, the validity and accuracy of the experimental procedure were examined.

As a typical example of experimental results, Figure 5 shows the change in the temperature of the standard material bed and sample bed with time. Figure 6 shows the relationship between the temperature difference between the standard material bed and sample bed and the temperature of the standard material bed. In this sample, the carbon composite iron ore hot briquets were mixed into ore bed by the amount of 20 mass% [CIO-B/(S+IO-P+CIO-B)]
As seen in Fig. 5, in the present experiment where the sample was solid packed bed, the temperature of the sample bed is increased in the same way as that of the standard bed. It is also seen in Figs. 5, 6 that the same measurement results for temperature as those in conventional differential thermal analysis are obtained. Accordingly, the starting temperature of the endothermic reaction for the sample bed is determined by extrapolation, namely, from the intersecting point of two tangential lines as shown in Fig. 6.

To examine the validity of the experimental procedure, a sample was taken from coke. The thermal reserve zone temperature in actual blast furnace of the coke was about 1000°C. The sample consisted only of the coke and was subjected to the same experiment as the above. However, only the gas composition above 1000°C was changed from that shown in Fig. 4 to the same composition as above 750°C, i.e. CO=37.5% and CO₂=12.5% so that the reaction could take place without iron ore. The starting temperatures obtained by three experiments were 1000°C, 1000°C, and 1009°C, which are consistent well with the thermal reserve zone temperature of the actual blast furnace. The reproducibility in three experiments was very good. From the above results, subsequent investigation was made on the assumption that the starting temperature of the endothermic reaction obtained by this procedure is approximately consistent with the thermal reserve temperature.

3.2. Lowering of Starting Temperature of Solution Loss Reaction by Adjoining Carbonaceous Material and Iron Ore

Given amount of the carbon composite iron ore hot briquets or the small size coke was mixed into the ore bed and the starting temperature of the endothermic reaction was measured. Fig. 7 shows the relationship between the starting temperature of the endothermic reaction equivalent to the solution loss reaction and the mass percentage of carbon in the ore bed [carbon/(S+IO-P+CIO-B+S-C)]. While the starting temperature of the endothermic reaction is about 1000°C when the sample consists only of coke, it decreases considerably when the carbon composite iron ore hot briquets or the small size coke is mixed into the ore bed. With the increase in the mixing ratio of carbonaceous material up to carbon content of 5 mass%, the starting temperature of reaction decreases remarkably. When the carbon content exceeds 5 mass%, the starting temperature remains almost constant. When compared with the same carbon content, the starting temperature of the endothermic reaction in the case of carbon composite iron ore hot briquets is fairly lower than that in the case of the small size coke. This is probably because the use of the carbon composite iron ore hot briquets has increased the degree of contact between carbonaceous material and iron ore in the ore bed. When the mixing ratio of carbonaceous material is low, significant deviation of measurement can be seen. This is probably because the positional relationship between carbonaceous material and thermocouple is not stable due to the small number of carbonaceous material or the carbonaceous material segregates in the ore bed.

Next, even when the small size coke is mixed into the ore bed, the starting temperature of the reaction decreases down to about 850°C by a temperature drop of about 150°C. On the other hand as has been shown in Fig.1, when the mixing ratio of the small size coke was increased from 30 kg/THM to 100 kg/THM, the decrease of thermal reserve zone temperature of the actual blast furnace was about 50°C. This is smaller than the temperature drop in the present experi-

Fig. 5. Temperature and time curve.

Fig. 6. Relationship between difference of temperature and temperature.

Fig. 7. Relationship between starting temperature of endothermic reaction and carbon content in ore bed.
ment. One explanation for this difference may be as follows: While small size coke with grain diameter of 8–32 mm was used in the actual blast furnace, the small size coke with the diameter of 9.5–13.2 mm was used in the present experiment and, as a result, the use of finer size coke increased the degree of contact between carbonaceous material and iron ore. This implies that, in order to lower the starting temperature of the reaction furthermore, it would be effective to make small size coke finer. However, if the grain diameter of the small size coke is made finer than 8 mm, the small size coke begins to fluidize at the throat of actual blast furnace. Accordingly, it can’t be expected to further lower the starting temperature of the reaction by decreasing the grain diameter of the small size coke. Another process to lower the starting temperature of the reaction furthermore might be to mix high reactivity coke into ore bed.\textsuperscript{12)}

Next, the intersecting point of the borderline of Fe–FeO and the curve for the solution loss reaction is about 700°C as can be seen in the equilibrium diagram of Fe–C–O system shown in Fig. 1. This temperature is considered to be the lower limit of the thermal reserve zone temperature in the blast furnace, because the indirect reduction reaction and the solution loss reaction are interactive and the major reactions in the actual blast furnace where coke is used as reducing agent. On the other hand, if carbon composite iron ore agglomerate is used, it is possible that the direct reduction reaction due to the solid carbon takes place and, as a result, the thermal reserve zone temperature can be decreased furthermore. Because the carbon composite iron ore hot briquets produce high degree of contact between carbonaceous material and iron ore, its use made it possible to lower the starting temperature of the solution loss reaction down to about 730°C, a temperature close to the above time shown in Fig. 1. This temperature is considered to be the lower limit. However, further temperature decrease could not be achieved in the present experiment. This is supposedly because the distance between carbonaceous material and iron ore in the briquets is increased during the reduction process from Fe$_2$O$_3$ to Fe$_3$O$_4$ and FeO and, consequently, the reduction reaction from FeO to Fe is proceeded mainly as indirect reduction reaction. Nevertheless, when briquets are used, even though the mixing ratio of briquets is a comparatively low value of about 20 mass%, low thermal reserve zone temperature is obtained as is the case with 100 mass%. This implies that the carbon composite iron ore hot briquet is a promising raw material for the control of the thermal reserve zone temperature of the blast furnace.

From the above results, it was found that the starting temperature of the solution loss reaction can be lowered by mixing carbon composite iron ore hot briquets or small size coke into conventional blast furnace raw material to adjoin carbonaceous material and iron ore, and that the starting temperature of the reaction can be lowered furthermore by increasing the degree of contact between carbonaceous material and iron ore. It was also found that, to realize the above result, the use of carbon composite iron ore agglomerate is effective.

3.3. Decrease in Reducing Agents Rate by Lowering Thermal Reserve Zone Temperature

From the above paragraph, it was found that the starting temperature of the solution loss reaction can be lowered by mixing carbonaceous material into ore bed. Since the thermal reserve zone temperature of the blast furnace is approximately consistent with the starting temperature of the solution loss reaction, the decrease in the reducing agents rate due to the drop in the thermal reserve zone temperature was calculated using Rist model,\textsuperscript{11)} a material-heat balance model based on equilibrium theory. The base conditions for the calculation are as follows: pulverized coal rate = 201 kg/THM, coke rate = 286 kg/THM, reducing agents rate = 487 kg/THM, and thermal reserve zone temperature = 1000°C. Shaft efficiency is a constant of 1.0.

Figure 8 shows the results of calculation. When the thermal reserve zone temperature decreases from the base conditions, the reducing agents rate decreases linearly. With the decrease of 100°C in the thermal reserve zone temperature, the reducing agents rate decreases by the amount of 19 kg/THM. As has been shown in Fig. 7, the use of the carbon composite iron ore briquets lowered the starting temperature of the endothermic reaction from 1000°C down to 730°C by 270°C. It is possible that the use of the carbon composite iron ore briquets may decrease the reducing agents rate by 51 kg/THM. Even when the carbon composite iron ore briquets of small amount of the order of 20 mass% is mixed into the ore bed, it is very effective as seen in Fig. 7. Therefore, it is a very promising means to decrease the blast furnace reducing agents rate.

In the above, it was found that by mixing carbonaceous material into ore bed to increase the degree of contact between carbonaceous material and iron ore, the reducing agents rate can be decreased considerably. What remains to be done is to make investigations based on kinetics, i.e. to quantify the change of shaft efficiency and the improvement in CO gas utilization efficiency due to the decrease in thermal reserve zone temperature.

4. Conclusion

The improvement in the efficiency and the decrease in the temperature of reactions in the blast furnace are required. Among the reactions, the solution loss reaction is an
intensive endothermic reaction and controls overall reaction inside the furnace, and the starting temperature of the solution loss reaction is approximately consistent with the thermal reserve zone temperature in the blast furnace. Therefore, to meet the above requirement, a technology to lower the starting temperature of the solution loss reaction by mixing various types of carbonaceous materials into blast furnace packed ore bed to adjoin carbonaceous materials and iron was fundamentally investigated. The following results were obtained.

(1) An experimental procedure, based on the principle of differential thermal analysis, to measure the starting temperature of the endothermic reaction equivalent to the solution loss reaction of packed bed was developed.

(2) By mixing carbonaceous material into the ore bed to adjoin carbonaceous material and iron ore, the starting temperature of the reaction could be lowered. With the increase in the amount of carbonaceous material mixed into the ore bed, i.e. the carbon content in the ore bed, the starting temperature of the reaction is lowered. When the carbon content in the ore bed is constant, with the increase in the degree of contact between carbonaceous material and iron ore, the starting temperature of the reaction is lowered.

(3) Since the carbon composite iron ore hot briquets provide high degree of contact between carbonaceous material and iron ore, when the carbon composite iron ore hot briquets are mixed into the ore bed, the starting temperature of the reaction is lowered remarkably as compared with the case of small size coke. In addition, even when the carbon composite iron ore hot briquets are mixed in small amount, the starting temperature is lowered remarkably.

(4) Therefore, by mixing carbonaceous material into the ore bed to increase the degree of contact between carbonaceous material and iron ore, even when the carbon content in the ore bed is low, the improvement in the CO gas utilization efficiency and the decrease in the reducing agents rate due to the considerable decrease in the thermal reserve zone temperature can be expected. To realize the above expectation, the use of carbon composite iron ore agglomerate is a promising means.

REFERENCES